CONDENSATION REACTIONS OF ARYL MESITOATES

BY
STANLEY BROOKE SPECK
B.S., Montana State College, 1937

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
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Introduction

The work of Morton and Peakes[1] suggested that, contrary to general belief, highly hindered esters might react with Grignard reagents under suitable conditions. These authors found that methyl 2,4,6-tribromobenzoate reacted with phenylmagnesium bromide to yield diphenyl-2,4,6-tribromophenylcarbinol.

The work of Bottorff[2] showed that reactions of alkyl mesitoates with alkylmagnesium halides did indeed occur and the present study deals with an examination of the reaction of aryl mesitoates with the Grignard reagent.

In this investigation three very different types of reactions were observed and accordingly the work falls naturally into three distinct sections which will be discussed under separate headings.

SECTION I. CONDENSATION OF ARYL MESITOATES WITH THE GRIGNARD REAGENT

Discussion and Experimental

The esters of mesitoic acid were prepared by condensing mesitoyl chloride with the proper phenol. Thus *p*-tolyl mesitoate was prepared from mesitoyl chloride and *p*-cresol.

It was found that alkylmagnesium halides condensed with aryl mesitoates in the 1,2 manner to give the corresponding mesityl alkyl ketone and the phenol. For example *p*-tolyl mesitoate with ethylmagnesium bromide produced propiomesitylene and *p*-cresol in good yield. The reactions were carried out at about 100°C.

The products obtained by the action of arylmagnesium halides on aryl mesitoates were more complex but in every case indicated that the formation of the mono-ketone was an intermediate step. For example, when *p*-tolyl mesitoate was treated with *p*-tolylmagnesium bromide, 2-(*p*-tolyl)-4-methyl-

benzoylmesitylene was obtained in a yield of about 13 percent. Apparently the ketone, 4-methylbenzoylmesitylene, is formed in the first step. It has been shown[3] that ketones of this type may react with Grignard reagents in such a manner as to suffer arylation in an *ortho* position.

This reaction with aryl Grignard reagents is apparently general. Thus α-naphthylmagnesium bromide and *p*-tolyl mesitoate gave 1-mesitoyl-2-(α-naphthyl)-naphthalene. The action of *m*-methoxyphenylmagnesium bromide on *p*-tolyl mesitoate produced 4,3′-dimethoxy-2-mesitoylbiphenyl. The product obtained from *o*-methoxyphenylmagnesium bromide and *p*-tolyl mesitoate was *o*-(*o*-methoxyphenyl)-benzoylmesitylene. The course of this reaction will be discussed in Section II.

p-Tolyl mesitoate was also treated with mesitylmagnesium bromide. Since *ortho* arylation could not occur, it was not surprising that dimesityl ketone was obtained. The yield, however, was rather low.

SECTION II. ORTHO ALKYLATION AND ARYLATION OF HINDERED DIARYL KETONES

Discussion and Experimental

The reaction (Section I) of *p*-tolyl mesitoate with *o*-methoxyphenylmagnesium bromide to give *o*-(*o*-methoxyphenyl)-benzoylmesitylene is unique and led to the discovery of a new and interesting reaction.

It appeared that this reaction proceeded in two steps, the first being the formation of *o*-methoxybenzoylmesitylene and the second the arylation of this ketone by replacement of the methoxyl group. As a test of this mechanism, *o*-methoxybenzoylmesitylene, which was prepared by condensing mesitoyl chloride with *o*-methoxyphenylmagnesium bromide, was treated with *o*-methoxyphenylmagnesium bromide. *o*-(*o*-Methoxyphenyl)-benzoylmesitylene was obtained in good yield. The reaction proceeded readily at room temperature. The action of phenylmagnesium bromide produced *o*-phenylbenzoylmesitylene.

It was shown that this reaction involving the replace-

ment of an *ortho* methoxyl group in a mesityl aryl ketone was general. Two other ketones, 4-methyl-2-methoxybenzoylmesitylene and 2-methoxy-1-mesitoylnaphthalene were prepared and both reacted readily with either alkyl- or arylmagnesium halides to produce the corresponding alkylated or arylated ketones in very good yields. The reactions proceeded rapidly and smoothly at room temperature.

SECTION III. PARA ACYLATION OF MESITYL ARYL KETONES

Discussion and Experimental

Alkylmagnesium halides and arylmagnesium halides that carry a substituent in the *para* position have been shown to condense with aryl mesitoates in the 1,2 manner to produce ketones (Section I). A much more remarkable result was obtained with arylmagnesium halides that had no substituent in the *para* position. *p*-Tolyl mesitoate and phenylmagnesium bromide, for example, yielded in addition to *p*-cresol a substance that proved to be *p*-dimesitoylbenzene.

The first step in this transformation must be the formation of benzoylmesitylene. The latter then condenses with unchanged mesitoic ester to produce the diketone. It was discovered that, in accordance with this scheme, the diketone could be made by condensing benzoylmesitylene with *p*-tolyl mesitoate.

Although this condensation is without parallel, it can be regarded as a Claisen reaction in which a *para* hydrogen atom is replaced by an acyl group. This point of view is supported by the fact that the condensation between the ketone and the ester can be effected with the aid of a number of alkaline catalysts. Among these are ethylmagnesium bromide, sodium and the binary mixture, Mg + MgI_2.[4] The latter afforded the best yields, which were about 50 percent of the theoretical amount.

By use of this reagent *p*-tolyl mesitoate was condensed with *m*-toluyl- and *m*-methoxybenzoylmesitylene and α-naphthoylmesitylene to yield the expected diketones. It is interesting that *o*- and *m*-tolylmagnesium bromides reacted with

p-tolyl mesitoate to yield the same diketone, 1,4-dimesitoyl-2-methylbenzene, which was identical with that produced from *m*-toluylmesitylene and *p*-tolyl mesitoate.

SUMMARY (SECTIONS I, II AND III)

The action of Grignard reagents on aryl mesitoates led to wholly unexpected results. It was found that alkylmagnesium halides converted the ester into the corresponding mesityl alkyl ketone in good yield.

The products obtained by the action of arylmagnesium halides on aryl mesitoates were more complex, but the first step appeared to be the formation of the ketone. Thus, *p*-tolylmagnesium bromide reacted with *p*-tolyl mesitoate to give *p*-cresol and 2-(*p*-tolyl)-4-methylbenzoylmesitylene.

o-Methoxyphenylmagnesium bromide reacted with *p*-tolyl mesitoate to give *o*-(*o*-methoxyphenyl)-benzoylmesitylene. A study of the mechanism of this reaction led to the discovery of a unique method of alkylation or arylation of *o*-methoxydiaryl ketones by use of the Grignard reagent.

It has been shown that certain mesityl aryl ketones undergo acylation in an unsubstituted *para* position when treated with aryl mesitoates. For example *p*-tolyl mesitoate converts benzoylmesitylene to *p*-dimesitoylbenzene. The reaction takes place under the influence of Grignard reagents, the binary mixture ($Mg + MgI_2$) and other alkaline catalysts.

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VITA

The author was born in Whitehall, Montana on January 28, 1916. He attended the public schools of that city and graduated from high school in 1933 when he entered Montana State College at Bozeman. He received the degree of Bachelor of Science in 1937 and held a position as Assistant Chemist at the Montana State Agricultural Experimental Station for one year. In the fall of 1938 he entered the graduate school of the University of Illinois where he was a teaching assistant in inorganic chemistry from 1938 to 1940 and a University fellow from 1940 to 1942.

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